

Aqueous Solution Properties of Poly(Trimethyl Acrylamido Propyl Ammonium Iodide) [Poly(TMAAI)]

WEN-FU LEE and CHAN-CHANG TSAI

Department of Chemical Engineering and Technology, Tatung Institute of Technology, Taipei, Taiwan, 10451, Republic of China

SYNOPSIS

The aqueous solution properties of a cationic poly(trimethyl acrylamido propyl ammonium iodide) [poly(TMAAI)] were studied by measurements of reduced viscosity, intrinsic viscosity, and flocculation test. The reduced viscosity and intrinsic viscosity of this cationic polyelectrolyte were related to the types and concentration of added salt. "Soft" salt anions were more easily bound on the quaternary ammonium (R_4N^+) of poly(TMAAI) than those of "hard" salt anions. Halide anions are hard anions; consequently, hard cations were more easily attracted to halide anions for reducing the binding degree of halide anion on the quaternary ammonium group (R_4N^+). Some salt ions were observed to strongly attract the quaternary ammonium of the cationic polymeric side chain for coagulation of the polymers. This effect would make the polymeric aqueous solution become turbid. The intrinsic viscosity behavior for cationic polyelectrolyte resulting from the electrostatic repulsive force of the polymer chain is contrasted with polyampholyte. A comparison of various flocculants as to the effect of flocculation was also studied. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The cationic monomers derived from dimethylamino alkyl acrylates and dimethylamino alkyl acrylamides have been widely used in the adhesive, coating, textile, hair conditioner, flocculant, and other related industries.¹⁻⁶ The functional groups on the side chain of the cationic polymers are usually ammonium group (primary, secondary, and tertiary amines and quaternary ammonium), sulfonium, and phosphonium.⁷ These cationic monomers with quaternary ammonium group are usually the quaternary ammonium group sites on the polymeric side chain.⁷⁻¹⁷ For example, Salamone et al. reported the synthesis of vinylimidazolium salts and their polymeric aqueous properties.^{8,9} The synthesis, aqueous solution properties, and application of cationic polyelectrolytes derived from acrylate were recently reported by several scholars.¹⁰⁻¹⁷

The effect of various salt ions on the interaction of polyelectrolytes in the aqueous solution has therefore been investigated by several scholars.¹⁸⁻³²

The site-binding interaction of salt ions and polymers by Huggins equation and Huggins constant k' was also investigated by several scholars.¹⁸⁻³² The counterion size was confirmed by them to have mitigated the degree of site binding for salt ion attracting polymers. Aqueous solution properties of the internal salt of poly [*N,N'*-dimethyl(acrylamido propyl) ammonium sulfonate] [poly(DMAAPS)] was reported in a previous study.³² The previous article concluded that soft salt anions and cations are more effective solubilizers than hard anions and cations. Some salt ions are strongly attracted by the quaternary ammonium group on the cationic polymeric side chain. This phenomenon causes the polymer to coagulate. This effect would cause the polymeric aqueous solution to become turbid, as observed in the present article. The difference of solution properties between cationic polyelectrolyte [poly(TMAAI)] and polyampholyte [poly(DMAAPS)] is also interesting. The aqueous solution properties of poly(TMAAI), especially in intrinsic viscosity in the presence of various salts were discussed. Finally, the cationic polyelectrolyte was applied in the flocculation test of a bentonite sol system.

EXPERIMENTAL

Preparation of Trimethyl Acrylamido Propyl Ammonium Iodide (TMAAI)³³

In a 100-mL volume flask equipped with a stirrer, a cooler, and a thermometer, *N*-(3-dimethylamino-propyl)acrylamide (15.7 g, 0.1 mol) and butanone (20 g); the contents were stirred at 3°C. A mixture of iodomethane (14.2 g, 0.1 mol) and butanone (20 g) was added dropwise for 1 h. After completion of the addition, the mixture was stirred at the same temperature for 7 h and then allowed to stand at 5°C for 2 days. The yellow solution was removed by filtration and the precipitated white crystals were washed with dry butanone several times, and dried in darkness and under reduced pressure for 24 h. The desired monomers were recovered and their purities were checked by melting point and elemental analyses (mp: 148°C; yield: 96%).

Elemental analysis (C₉H₁₉N₂OI): Calcd: C, 36.45%; H, 6.18%; N, 9.40%.

Found: C, 36.24%; H, 6.37%; N, 9.40%.

During the syntheses of TMAAI, the products became yellow from the irradiation of light and the existence of impurities in the solution. When the yellow product was washed with butanone to recover white crystals, the yield of synthetic monomer was diminished.

Preparation of Poly(Trimethyl Acrylamido Propyl Ammonium Iodide) [Poly(TMAAI)]³²

The monomer (TMAAI) aqueous solution (0.8M, 30 mL) and 4,4'-azobis(4-cyanovaleric acid) (ACVA) (1 g) were charged into an ampoule (100 mL) that was covered with aluminum foil. The cationic monomers were polymerized similarly to the sulfobetaine monomers. The polymer product was precipitated with a mixture of propanol-2 and diethyl ether (3 : 2), and dried for 24 h at 70°C under vacuum in darkness. Yield, 95%; *T_g*, 188.4°C.

Viscometric Measurements

Viscometric measurements were carried out with an Ubbelohde viscometer (the viscometer has a flow time of 76.23 s in the deionic water with 18 MΩ) at 30.00 ± 0.01°C. The polymer samples were dissolved in the salt concentration for yielding a stock solution of approximately 0.2 g/25 mL solvent.

Viscosity data were calculated by the Mark-Huggins equation:

$$\frac{\eta - \eta_0}{\eta_0 C} = \frac{\eta_{sp}}{C} = [\eta] + k' [\eta]^2 C \quad (1)$$

Flocculation Measurement

The extent of flocculation was determined by measurement of the transmittance of the supernatant. The tests, called Jar Test, were carried out in 1-L graduated cylinders (the basal area and height of the cylinders for every flocculation test are the same). The different concentrations of bentonite solution (1 L) were added to the cylinder. A stirring bar was vertically inserted into the cylinder, and the solution was stirred at a constant speed of about 150 rpm. The various amounts of different flocculants were added in the cylinder, and the mixture solution was then next stirred for 10 min. Once the solution had remained undisturbed for 10 min, the sludge volume was tested and the transmittance of upper limpid aqueous solution was measured by JASCO Model UVIDEC-5 visible spectrophotometer every 10 min. Deionic water was used as a standard solution (100%).

RESULTS AND DISCUSSION

Viscosity Measurement

Polyelectrolytes normally exhibit properties in solution that are quite different from general polymers. They are ionized in aqueous solution; the mutual repulsion of their charges causes expansions of the chain. The size of the polyelectrolyte random coil is a function of the concentrations of polymer and added salt, since both influence the degree of ionization. The property of viscosity is strongly affected by chain expansion. The reduced viscosity may even increase markedly as polymer concentration decreases, with consequent increase in the degree of ionization of the polymer. On the other hand, the addition of low-molecular-weight electrolyte (salt) to the aqueous solution increases the ionic strength of the solution outside the polymer coil relative to that inside, and also reduces the thickness of the layer of "bound" counterions around the chain. Those effects cause the chain to contract.³⁴ In our experiments, the poly(TMAAI) side chains would bear positive charges since the iodine ions became ionized in an aqueous solution. In this situation, the behavior of reduced viscosity exhibited a typical plot in the pure water is shown in Figure 1. This result shows the reduced viscosity in a higher concentration region increases with an increase of polymeric concentration due to the interaction of polymer chain and the reduced viscosity in a lower concentration region increases with a decreases of polymeric concentration. These phenomena were also observed by Salamone et al.^{8,9} and Liaw et al.¹⁵ for

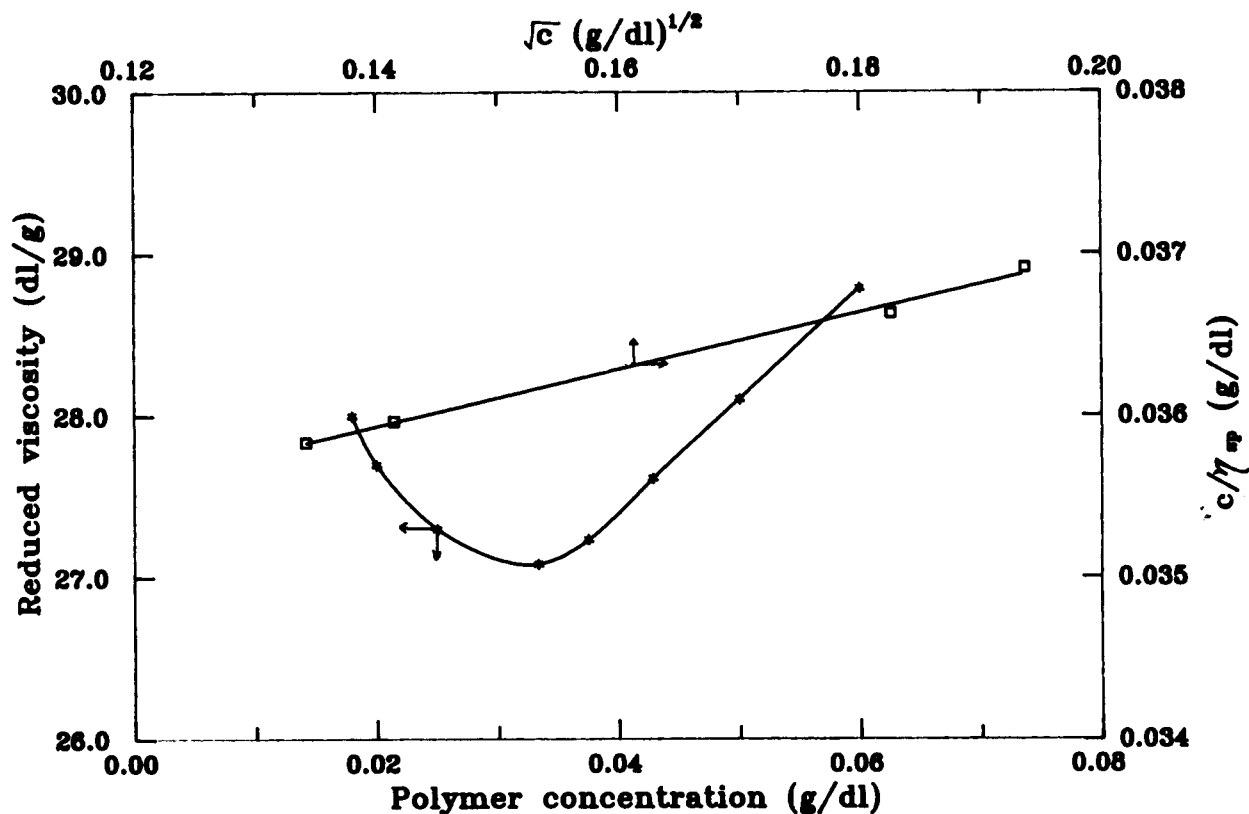


Figure 1 Reduced viscosities of poly(TMAAI) in H₂O.

various polyelectrolytes. As shown by the plot of reciprocal reduced viscosity versus square root of polymeric concentration, the concentration dependence of the reduced viscosity conforms to the Fuoss equation, $\eta_{sp}/c = A/(1 + B\sqrt{c})$, where A corresponds to intrinsic viscosity $[\eta]$, B is a constant related to an interaction of counterions with polyion, and c is polymeric concentration, in the lower polymeric concentration region.

Effect of Various Salts on Intrinsic Viscosity of Poly(TMAAI) in Aqueous Solution

The addition of salt to the aqueous solution of polyelectrolyte causes the polymeric chain to contract and decrease the intrinsic viscosity as mentioned above. Investigation of the influence of various salts on this effect and interpretation of charged neutralization and Pearson theory will therefore be presented in the following section.

Influence of Different Cations with a Common Anion (Cl⁻) on Intrinsic Viscosity of Poly(TMAAI)

The intrinsic viscosity $[\eta]$ and Huggins constant k' can be calculated from Figures 2 and 3 and Eq. (1).

The data shown in Table I and Table II exhibited an increase of the intrinsic viscosity in the order of $\text{Li}^+ > \text{Na}^+ > \text{K}^+$ for LiCl, NaCl, and KCl, and in the order of $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+}$ for MgCl₂, CaCl₂, and SrCl₂, respectively, for poly(TMAAI) in 0.5M aqueous salt solution.

These phenomena are contrasted with polyampholyte behavior.^{15,32} These results coincide with the Pearson principle, which states that hard acid species prefer binding with a hard base species and soft acid species prefer binding with a soft base species (the hard species, both acids and bases, tend to be smaller and slightly polarizable species; soft acids and bases tend to be larger and more polarizable species).³⁵ The hard acid species, e.g., chloride ion (Cl⁻), are easily bound to small radius hard bases, lithium ion (Li⁺). Hence, the lithium ion (magnesium ion) is more easily attracted to chloride ion than sodium ion and potassium ion (calcium ion and strontium ion). This result would reduce the site-binding degree of chloride ion (Cl⁻) on the quaternary ammonium group (R₄N⁺) and also decrease the degree of the chloride ion (Cl⁻) neutralizing the positive charge on polymeric side chains for poly(TMAAI). This result yields a higher intrinsic viscosity in an aqueous salt solution.

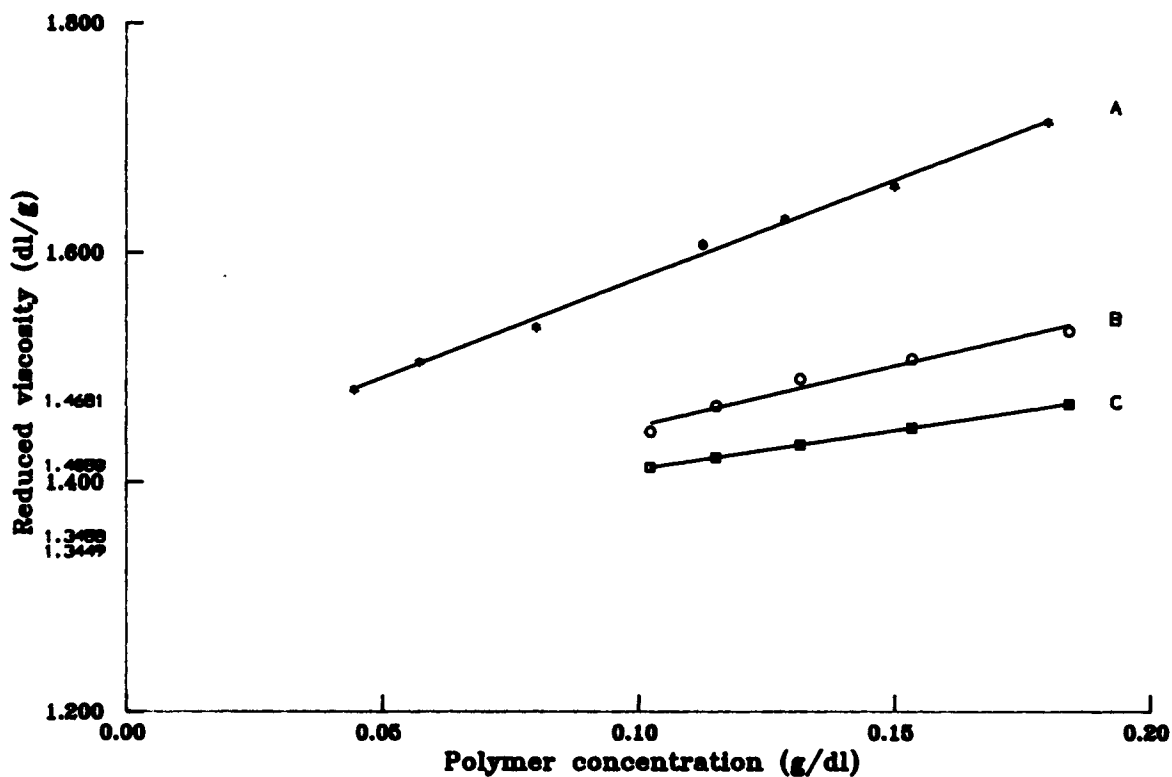


Figure 2 Reduced viscosities of poly(TMAAI) as a function of concentration for salts containing common anion: (A) 0.5M LiCl, (B) 0.5M NaCl, and (C) 0.5M KCl.

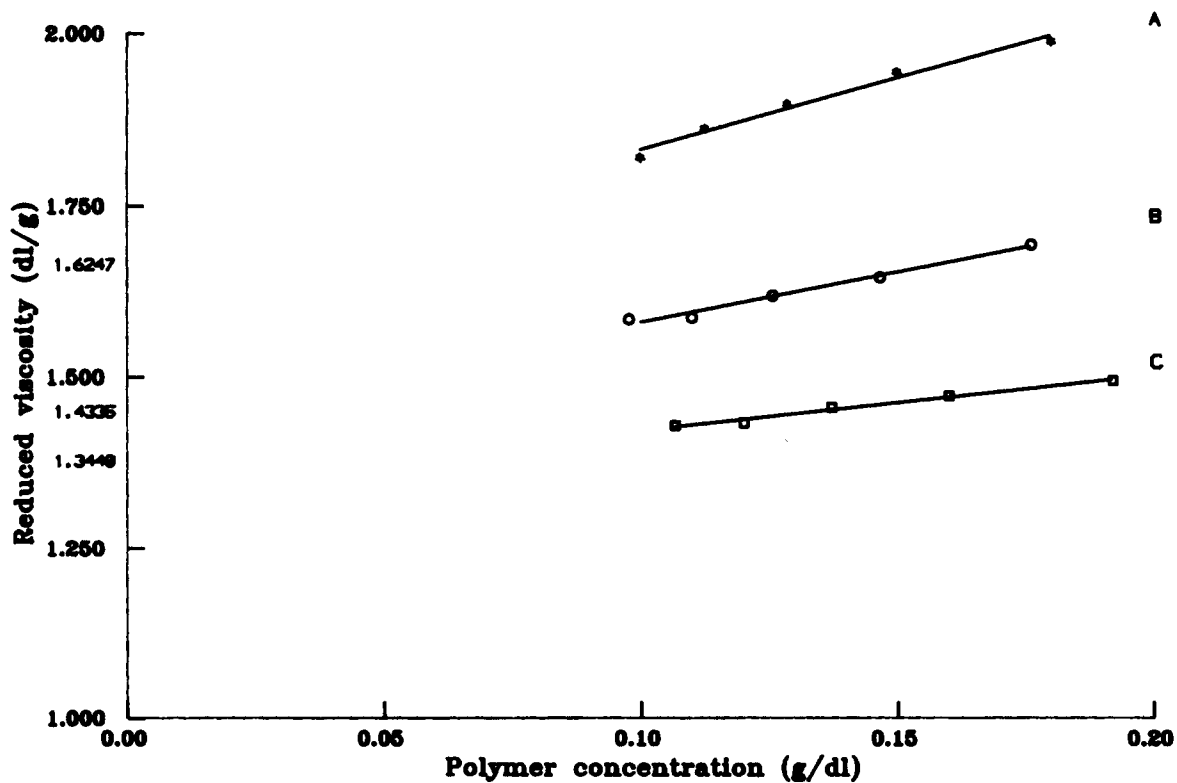


Figure 3 Reduced viscosities of poly(TMAAI) as a function of concentration for salts containing common anion: (A) 0.5M MgCl₂, (B) 0.5M CaCl₂, and (C) 0.5M SrCl₂.

Table I Effect of Various Monovalent Cations on the Viscosity Behavior of Poly (TMAAI) at 30°C

Salt Solution (0.5 M)	Slope	$[\eta]$	k'
LiCl	1.73	1.40	0.88
NaCl	1.04	1.35	0.58
KCl	0.67	1.34	0.37

Influence of Different Anions with a Common Cation (K^+ or Na^+) on Intrinsic Viscosity of Poly(TMAAI)

The data shown in Figure 4 and Table III display an increase of the intrinsic viscosity for monovalent anions in the order of $Cl^- > Br^- > I^-$ for KCl, KBr, and KI, respectively, for poly(TMAAI) in 0.5M aqueous salt solution. This is because the larger anion with common positive charge (charge density is smaller) is easily polarized and bound to quaternary ammonium group (R_4N^+) on poly(TMAAI). The positive charge on polymeric side chains could therefore become effectively neutralized by the larger anion and reduced the intrinsic viscosity of

Table II Effect of Various Divalent Cations on the Viscosity Behavior of Poly (TMAAI) at 30°C

Salt Solution (0.5 M)	Slope	$[\eta]$	k'
$MgCl_2$	2.08	1.62	0.79
$CaCl_2$	1.48	1.43	0.72
$SrCl_2$	0.80	1.34	0.44

poly(TMAAI) in 0.5M aqueous salt solution. This result corresponds with the Pearson principle.

For the various acidic groups, the data listed in Figure 5 and Table IV show an increase of the intrinsic viscosity for poly(TMAAI) in 0.5M aqueous salt solution in the order of $ClO_3^- < NO_2^- < SO_4^{2-} < CH_3COO^-$ for $NaClO_3$, $NaNO_2$, Na_2SO_4 , and CH_3COONa , respectively. This tendency is similar to the monovalent anions (Fig. 4 and Table III). The poly(TMAAI) does not dissolve in 0.5M Na_2ClO_4 and $NaNO_3$ aqueous solution. This phenomenon is attributed to the polymeric side chains of poly(TMAAI) being attracted by salt counterions (ClO_4^- and NO_3^-), and this attraction causes the polymeric chain not to expand and agglomerate in

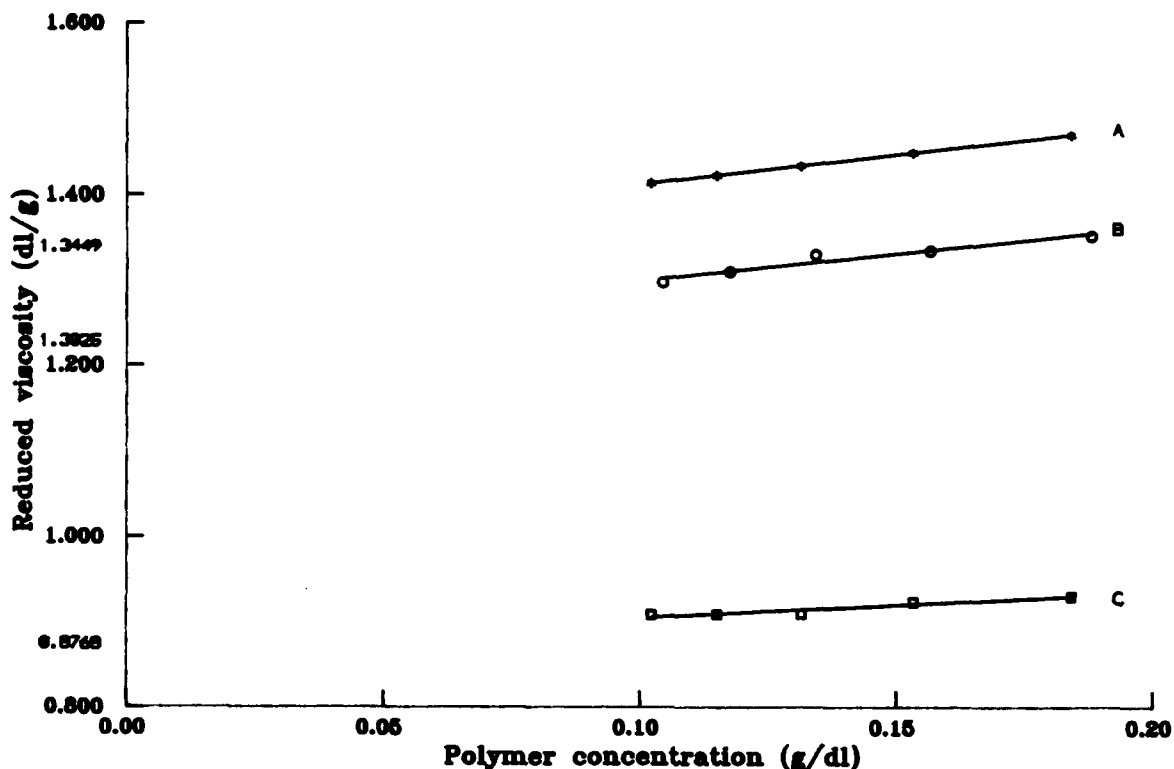

Figure 4 Reduced viscosities of poly(TMAAI) as a function of concentration for salts containing common cation: (A) 0.5M KCl, (B) 0.5M KBr, and (C) 0.5M KI.

Table III Effect of Various Anions on the Viscosity Behavior of Poly (TMAAI) at 30°C

Salt Solution (0.5 M)	Slope	$[\eta]$	k'
KCl	0.67	1.34	0.37
KBr	0.64	1.23	0.42
KI	0.29	0.88	0.38

this situation. The sulfate ion (SO_4^{2-}) has a higher charge density, which was difficult to be polarized during sulfate ion nearing the quaternary ammonium group (R_4N^+). Binding to a quaternary ammonium group (R_4N^+) is therefore difficult. (The sulfate ion is regarded as a hard base species in Pearson principle because of its higher charge density). The acetate ion (CH_3COO^-) is a weak acidic group and is easily associated in forming an acetic acid in aqueous solution. Therefore, the ionic intensity is very small and can not effectively neutralize the charges of the polycations. The intrinsic viscosity of poly(TMAAI) was, thus, higher than other anions in the 0.5 M aqueous salt solution. The results

Table IV Effect of Various Acidic Groups on the Viscosity Behavior of Poly (TMAAI) at 30°C

Salt Solution (0.5 M)	Slope	$[\eta]$	k'
NaClO_4	—	—	—
NaNO_3	—	—	—
NaClO_3	0.66	1.30	0.39
NaNO_2	0.45	1.43	0.22
Na_2SO_4	1.36	1.49	0.62
Na_2CO_3	1.67	1.56	0.68
CH_3COONa	0.90	1.82	0.27

from the above-mentioned results obtained from different anions and various acids for poly(TMAAI) are also contrasted with polyampholyte.^{15,32}

For the various divalent acidic groups, the data (See Figure 6 and Table V) showed an increase of the intrinsic viscosity for poly(TMAAI) in 0.5 M aqueous salt solution in the order of $\text{CO}_3^{2-} > \text{SO}_4^{2-} > \text{SO}_3^{2-}$ ($\text{S}_2\text{O}_3^{2-}$) for Na_2CO_3 , Na_2SO_4 , and Na_2SO_3 ($\text{Na}_2\text{S}_2\text{O}_3$), respectively. This tendency is also corresponded with Pearson principle.

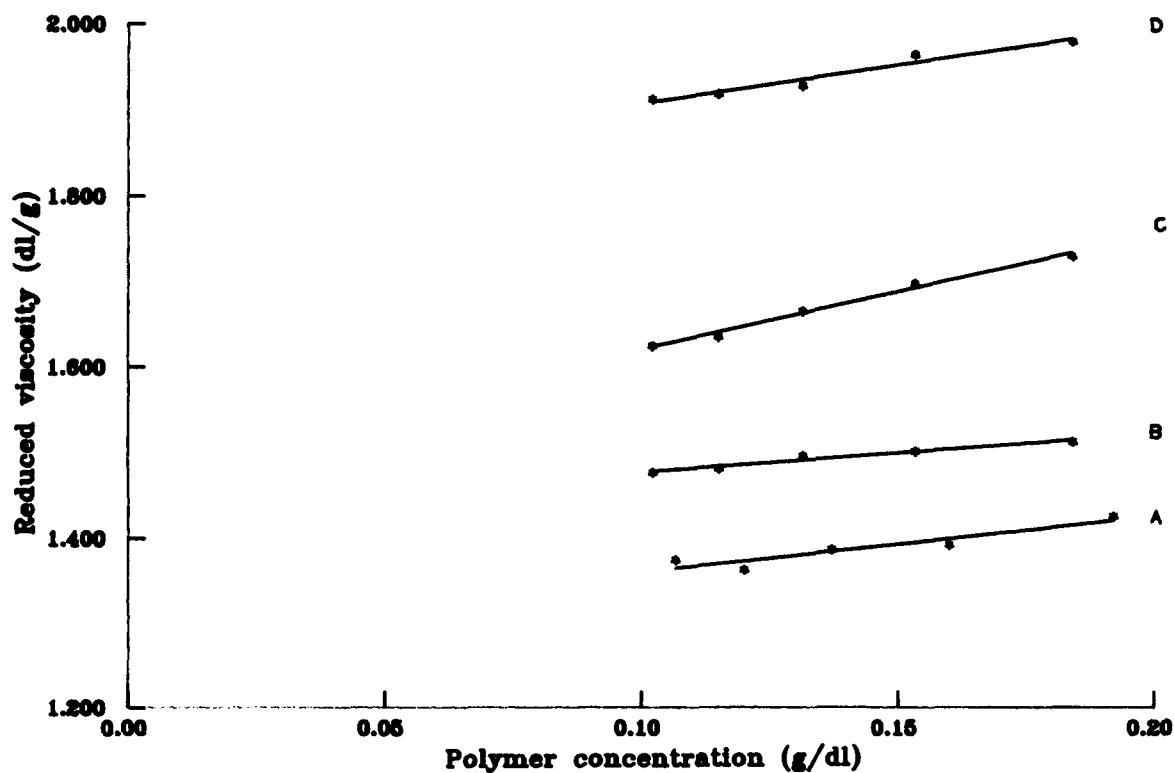
**Figure 5** Reduced viscosities of poly(TMAAI) as a function of concentration for acidic ions. (A) NaClO_3 , (B) NaNO_2 , (C) Na_2SO_4 , and (D) CH_3COONa .

Table V Effect of Various Divalent Acidic Groups on the Viscosity Behavior of Poly (TMAAI) at 30°C

Salt Solution (0.5 M)	Slope	$[\eta]$	k'
Na ₂ CO ₃	1.67	1.56	0.68
Na ₂ SO ₄	1.36	1.49	0.62
Na ₂ S ₂ O ₃	0.97	1.42	0.48
Na ₂ SO ₃	1.82	1.37	0.97

Effect of Various Salt Concentrations in Aqueous Solution on the Intrinsic Viscosity of Poly(TMAAI)

The presumed concept of chain contraction the cationic polymers for salt ions attracting or site binding on the polymers was corrected. Therefore, the phenomenon of a decrease of reduced viscosity with an increase of salt concentration could perhaps be rationalized. The effect of various NaCl concentrations between 0.05 and 1 mol/L on reduced viscosity is illustrated in Figure 7 for the poly(TMAAI). A significant decrease in reduced viscosity apparently

occurred with an increasing of the NaCl concentration. These phenomena are greatly contrasted with the inner salt of (polysulfobetaines).^{31,32}

When the salt concentration is increased, a partial amount of negative charges of salt would become site-bound on the quaternary ammonium group (R₄N⁺) on the poly(TMAAI). The polymeric charges would become neutralized by the counterions in the aqueous solution. This occurrence would reduce the repulsion of polymeric side chains for the sake of both decreasing the extent of tightly stretched chains and also coiling the polymeric main chains. The chloride ions (Cl⁻) binding on quaternary ammonium group (R₄N⁺) of poly(TMAAI) were increased in high salt concentration to form regions of high local charge density.

The slope, intrinsic viscosity, and Huggins constant k' shown in Table VI could be calculated through Figure 7 and Eq. (1). The values for the Huggins constant k' increase with a decrease of the intrinsic viscosity as the concentration of the salt was increased.

These phenomena might be due to the fact that the addition of salt can loosen the compact structure that resulted from the inter- and intramolecular

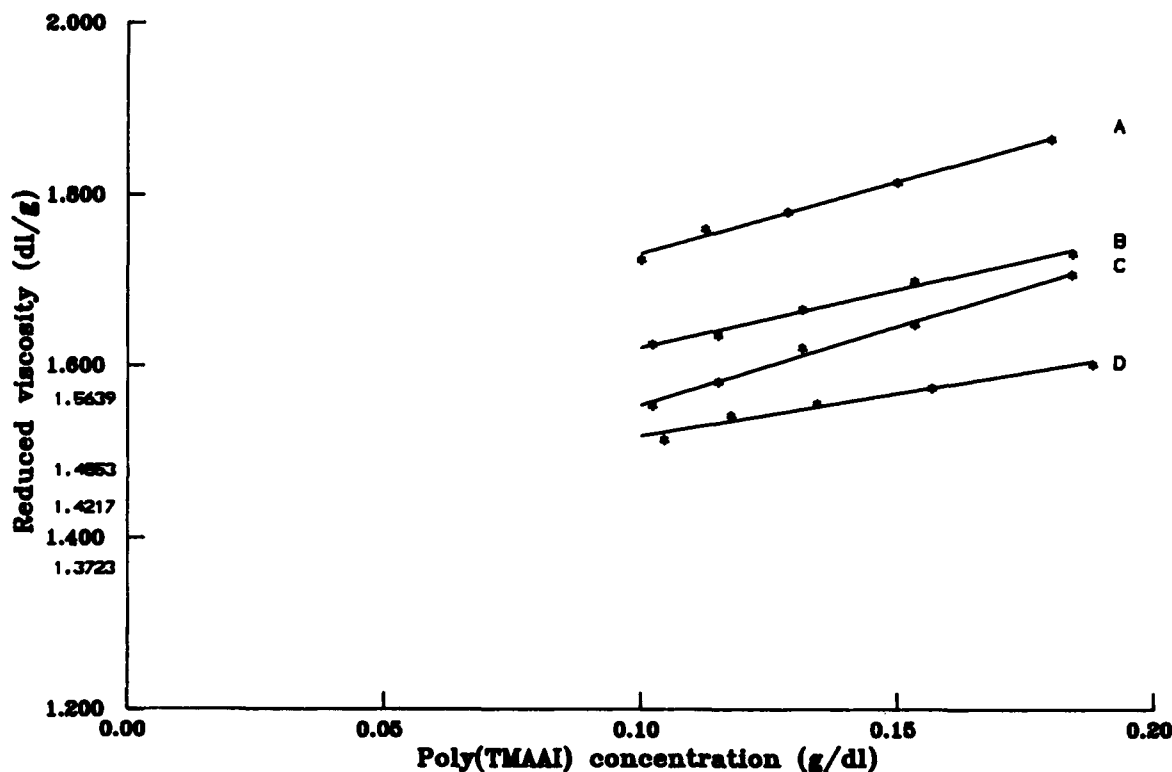


Figure 6 Reduced viscosities of poly (TMAAI) as a function of concentration for various divalent acidic groups. (A) 0.5M Na₂CO₃, (B) 0.5M Na₂SO₄, (C) 0.5M Na₂SO₃, and (D) 0.5M Na₂S₂O₃.

Table VI Effect of NaCl Concentrations on the Intrinsic Viscosity and Huggin's Constant of Poly (TMAAI) at 30°C

NaCl Concentration	Slope	$[\eta]$	k'
0.05 M	2.08	3.00	0.31
0.10 M	2.17	2.36	0.39
0.30 M	1.17	1.67	0.42
0.50 M	0.92	1.42	0.43
0.70 M	0.82	1.36	0.44
1.00 M	0.80	1.34	0.45

ionic interactions, and, thus, the polymer can behave more freely in the salt solution.^{15,36} In other words, the higher the salt concentration is, the lower is the electrostatic repulsive force and, thus, the lower the intrinsic viscosity. This result was also observed by Liaw,¹⁵ Conway,³⁷ and Eisenberg and Pouyet.¹⁰ The intrinsic viscosity $[\eta]$, obtained by extrapolating the curves of Figure 7, at constant simple electrolyte concentration to zero concentration of the polymer, are plotted in Figure 8 as a function of the reciprocal square root of the ionic strength ($1/\sqrt{c_s}$).

The intrinsic viscosity of polyelectrolyte is often

expressed by the general law.^{38,39}

$$[\eta] = k_1 + k_2(1/\sqrt{c_s})$$

For polyacrylamide, as previous observed,⁴⁰ the viscosity is practically independent of the ionic strength. In fact, in our case, no linear relationship between $[\eta]$ and $C_s^{-1/2}$ is observed (see Fig. 8). This peculiar behavior of our samples might be explained in terms of the bulkiness of the side chain in the vinylic backbone. These would hinder the free flowing of solvent molecules around the chains. This occurrence was also observed by Mabire,¹³ Kawagawa,¹⁶ and Imai,⁴¹ for various polyelectrolytes.

Flocculation Measurement

The charged surface of colloids forms the electrical double layer in aqueous solution because either the ions have cohered on the surface of colloids or the charges have ionized from the deficiently crystalline structure of colloids. The charges of colloidal surface for general clay produce a negative charge, which causes the mutual repulsion of the colloids in forming turbid suspension aqueous solution and not to be flocculated. For conventional flocculational

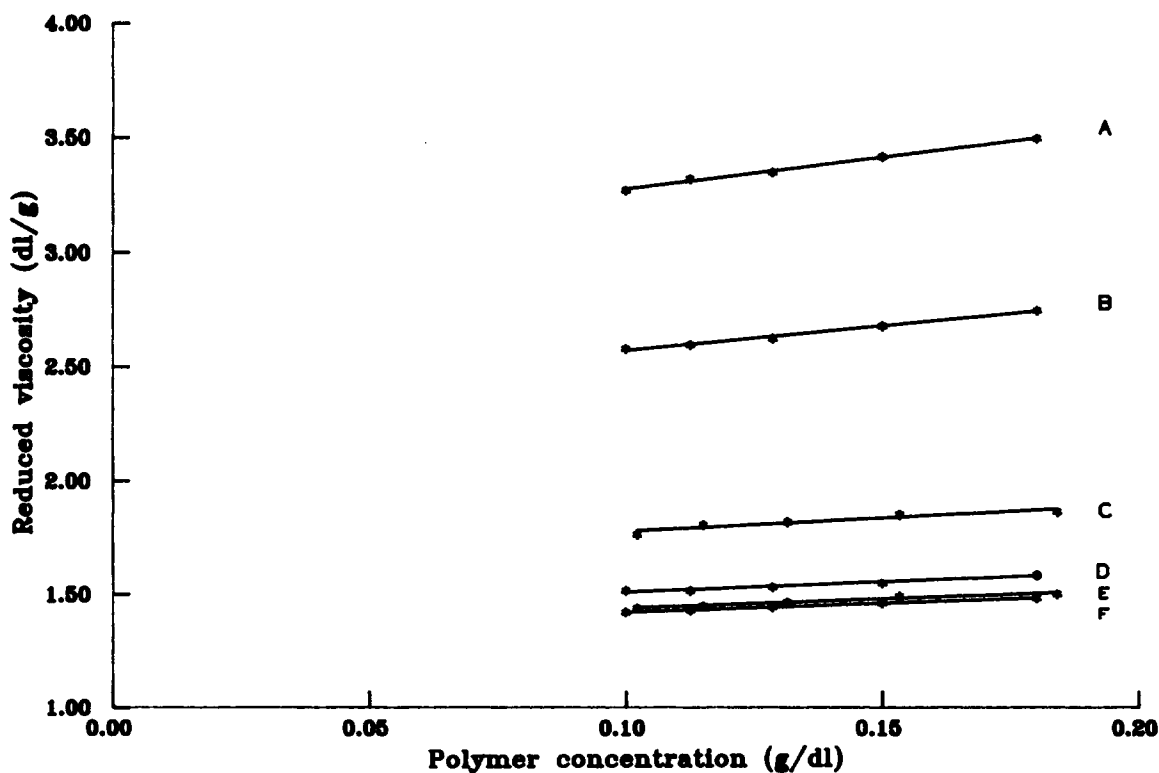


Figure 7 Reduced viscosities of poly(TMAAI) as a function of concentration for NaCl: (A) 0.05M, (B) 0.10M, (C) 0.30M, (D) 0.50M, (E) 0.70M, and (F) 1.00M.

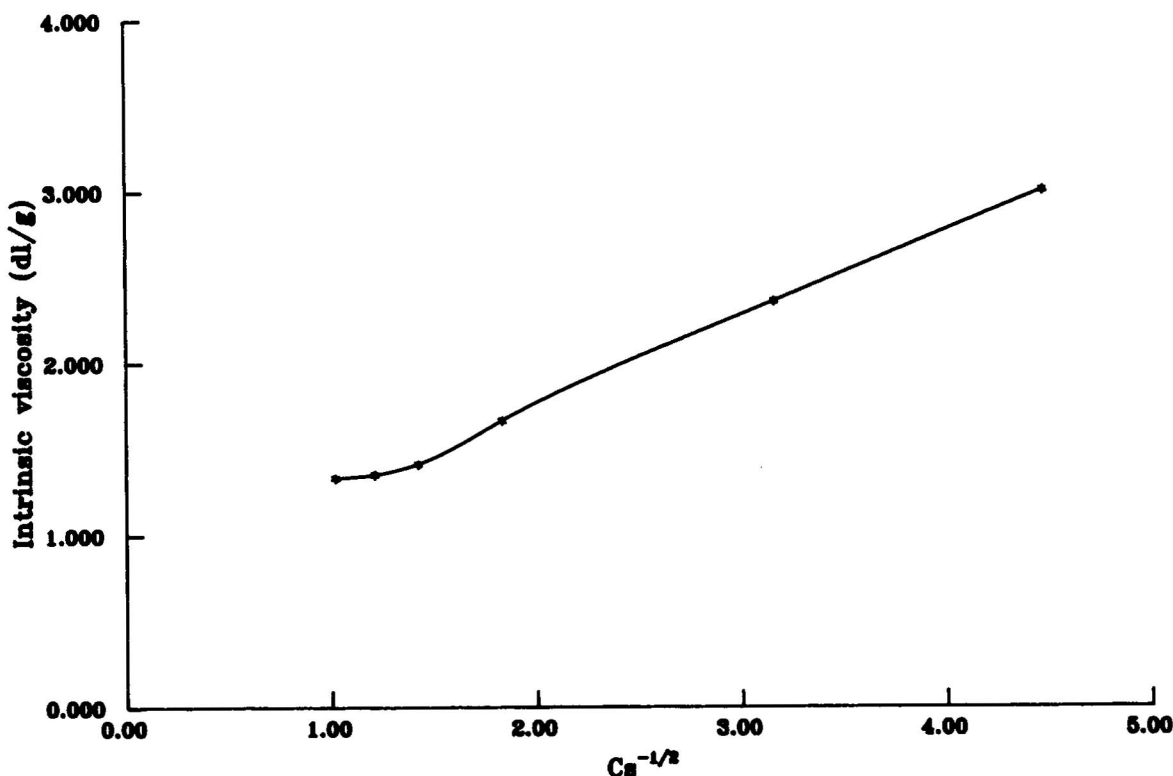


Figure 8 Intrinsic viscosities of poly(TMAAI) as a function of reciprocal square root of ionic strength.

methods, the added trivalent cations can neutralize the charge of colloids for the sake of both reducing the mutual repulsion of the charges on colloidal surface and also coagulating colloids. The colloids would become flocculated whenever polyelectrolyte was introduced into the suspension aqueous solution. The flocculation mechanism of polyelectrolyte coagulant was previously investigated by Ruehawein and Ward who explained the phenomenon of flocculation by chemical bridging.^{42,43}

Effect of Flocculation for Poly(TMAAI) and $Al_2(SO_4)_3$

Bentonite particles in a suspension aqueous solution absorb visible light, which consequently reduces the transmittance of the suspension solution shown in Figure 9 becomes decreased as the bentonite concentration is increased; however, this transmittance is a nonlinear depression between transmittance of suspension solution and bentonite concentration.

The influence of different coagulants on the transmittance and sludge volume of suspension solution with 1000 or 250 ppm bentonite concentration is shown in Figure 10. From the observed data the bentonite particles become flocculated when the

flocculant concentration reaches 60 (20) and 40 ppm (5 ppm) for $Al_2(SO_4)_3$ and poly(TMAAI) in 1000 ppm (250 ppm) bentonite solution, respectively. The residual bentonite concentration on the upper limpid aqueous solution is about 25 ppm and less than 5 ppm for $Al_2(SO_4)_3$ and poly(TMAAI) in 1000 ppm (250 ppm) bentonite solution, respectively. This event occurs since poly(TMAAI) neutralizes the charges of colloids, which consequently both reduces the distance of colloids and also forms large particles by secondary forces (Van der Waals forces). Additionally, the polymeric chains entangle the colloidal particles so as to increase the coagulation of colloids. Poly(TMAAI) is therefore capable (Fig. 11) of more rapidly coagulating the suspension than $Al_2(SO_4)_3$ in the initial period with 1000 ppm bentonite concentration. (The settling of various coagulants is very rapid in 250 ppm bentonite concentration. The settling of various coagulants is therefore similar.) The bulk sludge settled by poly(TMAAI) coagulant is difficult to condense. The sludge volume is therefore (Fig. 11) larger than that settled by $Al_2(SO_4)_3$.

The effect of flocculation for different molecular weights of poly(TMAAI) coagulant ($[\eta] = 7.5$ and 24.3) are indicated from Figures 10 and 11 to be

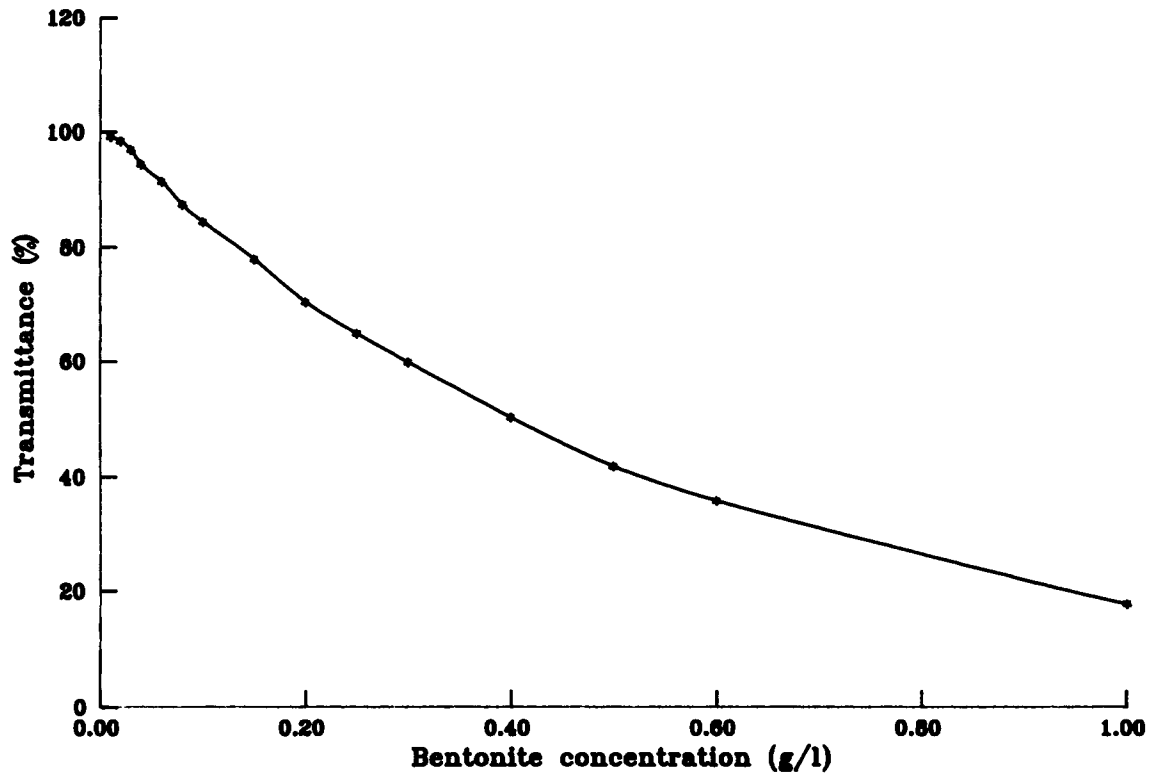


Figure 9 The transmittance of varied bentonite concentration.

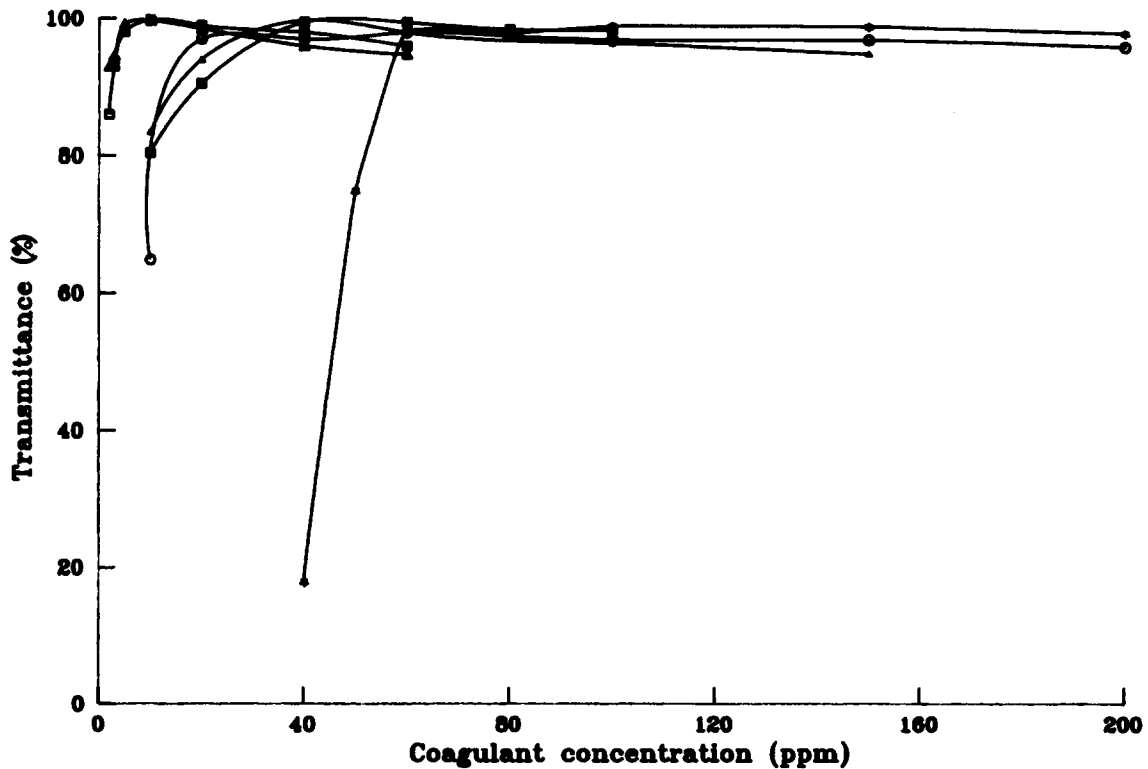


Figure 10 The transmittance vs. polymer concentration in bentonite aqueous solution: (*) transmittance of Al₂(SO₄)₃ in 1000 ppm bentonite; (■) transmittance of Poly(TMAAI) [η] = 7.5 in 1000 ppm bentonite; (▲) transmittance of Poly(TMAAI) [η] = 24.3 in 1000 ppm bentonite; (○) transmittance of Al₂(SO₄)₃ in 250 ppm bentonite; (□) transmittance of Poly(TMAAI) [η] = 7.5 in 250 ppm bentonite; (△) transmittance of Poly(TMAAI) [η] = 24.3 in 250 ppm bentonite.

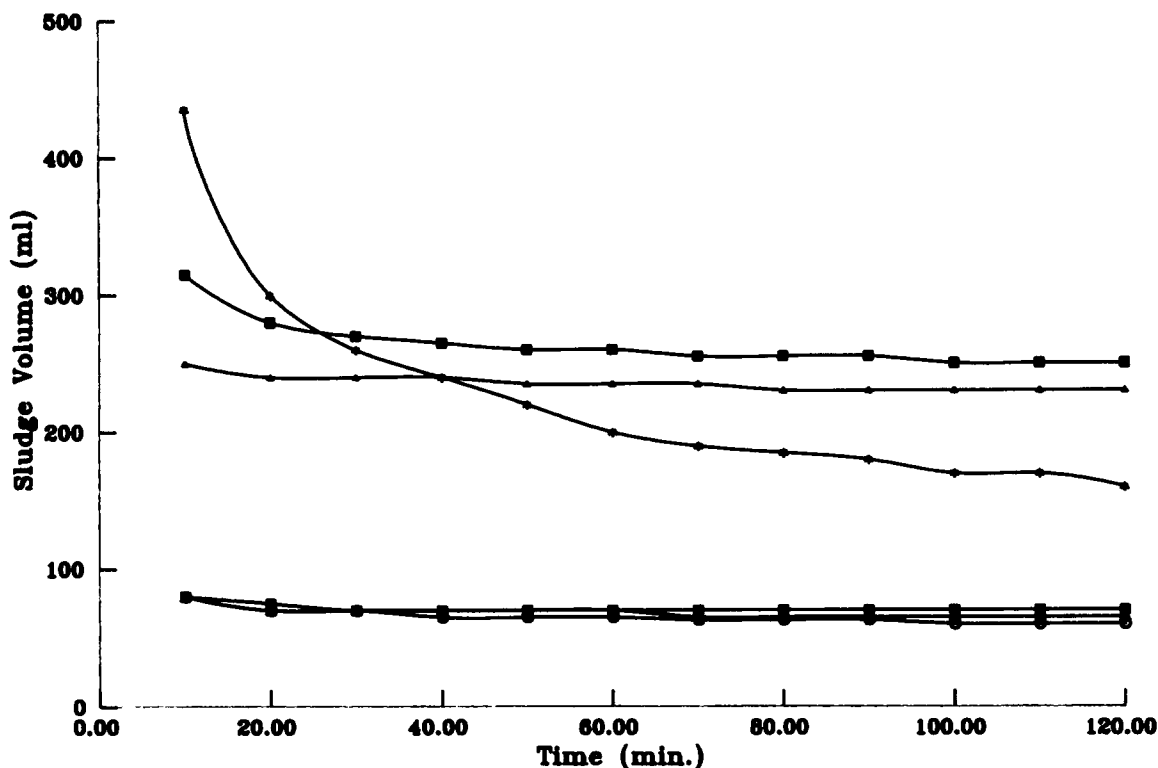


Figure 11 The sludge volume of varied coagulants (60 ppm) in bentonite aqueous solution: (*) $\text{Al}_2(\text{SO}_4)_3$ in 1000 ppm bentonite aqueous solution; (■) poly(TMAAI) $[\eta] = 7.5$ in 1000 ppm bentonite aqueous solution; (▲) poly(TMAAI) $[\eta] = 24.3$ in 1000 ppm bentonite aqueous solution; (○) $\text{Al}_2(\text{SO}_4)_3$ in 250 ppm bentonite aqueous solution; (□) poly(TMAAI) $[\eta] = 7.5$ in 250 ppm bentonite aqueous solution; (△) poly(TMAAI) $[\eta] = 24.3$ in 250 ppm bentonite aqueous solution.

similar. From the observed data the colloids are indicated to be coagulated and settled as the molecular weight of poly(TMAAI) reaches some degree of polymerization.⁴⁴

CONCLUSION

The behavior of aqueous solution properties of cationic polyelectrolyte would be evidently transferred as salts were added in polymeric aqueous solution. As the radius of salt ion was large, the degree of attracting poly(TMAAI) for salt and the degree of polymeric recoiled were increased and the reduced viscosity and intrinsic viscosity were decreased. As the salt concentration was increased, the intrinsic viscosity was decreased and Huggins constant k' was increased (Huggins constant k' was affected from polymer-solvent and polymer-polymer interaction). The poly(TMAAI) can more effectively and rapidly coagulate the suspension than $\text{Al}_2(\text{SO}_4)_3$; however, the sludge volume with poly(TMAAI) flocculant is

larger than that with $\text{Al}_2(\text{SO}_4)_3$. The colloids are available coagulated and settled as the molecular weight of poly(TMAAI) reaches something of a degree of polymerization.

REFERENCES

1. G. H. Boyd and M. Hayek, U.S. Pat. 2,723,246 (1955).
2. H. Ohtani, M. Ishii, A. Furuno, and Y. Wada, *Jpn. Kokai, Tokkyo Koho*, **50**, 117066 (1975).
3. Sanyo Chemical Industries, Ltd., *Jpn. Kokai Tokkyo Koho*, **58**, 144176 (1983).
4. R. Sugae and M. Kimura, *Jpn. Kokai Tokkyo Koho*, **53**, 130400 (1978).
5. T. J. Padden, Eur. Pat. Appl., Ep. 0,119,461 (1985).
6. K. J. Valan, U.S. Pat. 3,954,960 (1976).
7. M. F. Hoover, *J. Macromol. Sci.*, **A4**(6), 1327 (1970).
8. J. C. Salamone, S. C. Israel, P. Taylor, and B. Snider, *Polym. Prepr.*, **14**(2), 778 (1973).
9. J. C. Salamone, W. Volksen, S. C. Israel, D. C. Raia, A. Broggi, and T. D. Hsu, *Polym. Prepr.*, **16**, 731 (1976).

10. H. Eisenberg and J. Pouyet, *J. Polym. Sci.*, **13**, 85 (1954).
11. J. S. Tan and A. R. Sochor, *Macromolecules*, **14**, 1700 (1981).
12. S. M. Hamid and D. C. Sherrington, *Polymer*, **28**, 325 (1987).
13. F. Mabire, R. Audebert, and C. Quivoron, *Polymer*, **25**, 1317 (1984).
14. K. Nagai, Y. Ohishi, H. Inaba, and S. Kudo, *J. Polym. Sci.*, **23**, 1221 (1985).
15. D. J. Liaw, S. J. Shiau, and K. R. Lee, *J. Appl. Polym. Sci.*, **45**, 61 (1992).
16. I. Kagawa and R. M. Fuoss, *J. Polym. Sci.*, **18**, 535 (1955).
17. S. Subramanyam and A. Blumstein, *Macromolecules*, **25**, 4058 (1992).
18. A. Malliaris and C. M. Paleos, *J. Colloid Interface Sci.*, **101**(2), 364 (1984).
19. M. Nagasawa and I. Kagawa, *J. Polym. Sci.*, **25**, 61 (1957).
20. U. P. Strauss, D. Woodside, and P. Wineman, *J. Phys. Chem.*, **61**, 1353 (1957).
21. U. P. Strauss, *J. Am. Chem. Soc.*, **80**, 6498 (1958).
22. U. P. Strauss and S. Bluestone, *J. Am. Chem. Soc.*, **81**, 5292 (1959).
23. U. P. Strauss and P. D. Ross, *J. Am. Chem. Soc.*, **81**, 5295 (1959); *J. Am. Chem. Soc.*, **81**, 5299 (1959).
24. P. D. Ross and U. P. Strauss, *J. Am. Chem. Soc.*, **82**, 1311 (1960).
25. U. P. Strauss and Y. P. Leung, *J. Am. Chem. Soc.*, **87**, 1476 (1965).
26. H. P. Gregor, *J. Polym. Sci.*, **23**, 467 (1957).
27. L. Kotin and M. Nagasawa, *J. Chem. Phys.*, **36**(4), 873 (1962).
28. J. S. Tan and P. R. Marcus, *J. Polym. Sci., Polym. Phys. Ed.*, **14**, 239 (1976).
29. F. Osawa, N. Imai, and I. Kagawa, *J. Polym. Sci.*, **13**, 93 (1954).
30. I. Kagawa and H. Gregor, *J. Polym. Sci.*, **23**, 477 (1957).
31. D. J. Liaw, W. F. Lee, Y. C. Whung, and M. C. Lin, *J. Appl. Polym. Sci.*, **30**, 4697 (1985).
32. W. F. Lee, C. C. Tsai, *Polymer*, to appear.
33. W. F. Lee and C. C. Tsai, *Polymer*, to appear.
34. F. W. Billmery, Jr., *Textbook of Polymer Science*, Wiley, New York, 1984, p. 218.
35. J. E. Huheey, *Inorganic Chemistry*, Harper and Row, New York, 1972.
36. P. M. Budd, in *Comprehensive Polymer Science*, G. Allen, Ed., Pergamon Press, Oxford, 1989, Vol. 1, p. 226.
37. B. E. Conway, *J. Polym. Sci.*, **18**, 257 (1975).
38. D. T. F. Pals and J. J. Hermans, *J. Polym. Sci.*, **3**, 897 (1948).
39. I. Noda, T. Tsuge, and M. Nagasawa, *J. Phys. Chem.*, **74**, 710 (1970).
40. J. Eliassaf and A. Silbergberg, *J. Polym. Sci.*, **41**, 33 (1959).
41. N. Imai, Symposium on Polyelectrolytes and Charged Interfaces, Strasbourg, France, 1981.
42. P. C. Hiemenz, *Principles of Colloid and Surface Chemistry*, 2nd ed., Marcel Dekker, New York, 1986.
43. L. D. Benefield, J. F. Judkins, and B. L. Weand, *Process Chemistry for Water and Wastewater Treatment*, Prentice-Hall, Englewood Cliffs, NJ, 1982.
44. G. Durand-Piana, F. Lafuma, and R. Audebert, *J. Colloid Interface Sci.*, **119**(2), 474 (1987).

Received July 28, 1993

Accepted December 10, 1993